1 Glass like material with improved safety characteristics. 2 3 The present invention relates to a glass-like material 4 which has improved safety characteristics compared to 5 ordinary glass. 6 7 In the present Application references to a "glass-like" 8 material refer to a material having the following 9 characteristics; clarity, brittleness, low strain to 10 failure and rigidity. 11 12 Ordinary glass is used in a variety of everyday 13 applications. For example it is known in the art to use 14 glass as a protective covering over fire and other types of emergency alarms, emergency door releases, emergency 15 16 stop buttons on public transport, fire extinguishers, 17 fire axes and the like. As glass is transparent persons 18 can quickly and easily identify the presence of the alarm 19 or apparatus in the retaining box. If required, the 20 glass can be broken in order to access the alarm or 21 device. 22 23 However an inherent problem lies in the manner in which

the glass can be broken. Often a subsidiary device such

1 as a hammer is supplied with, or near to, the alarm or

- 2 apparatus, and can be used to break the glass. However,
- 3 in the event that this device is missing or cannot be
- 4 located in an emergency situation it will be necessary
- 5 for the person who wishes to access the apparatus or
- 6 alarm to break the glass by some other means. In the
- 7 event of an emergency situation the person may use, for
- 8 example, a hand or elbow for this purpose, and may, as a
- 9 result, sustain injuries from breaking the glass.
- 10 Breakage of glass results in the production of sharp
- 11 glass fragments and splinters, which can cause injury to
- 12 the user or other persons in the proximity of the alarm
- 13 or apparatus. In addition the potential risk of injury
- 14 from breaking the glass may cause hesitation on the part
- 15 of the person who wishes to access the alarm or
- 16 apparatus, having dangerous consequences.

17

- 18 The glass may also be broken by malicious or accidental
- 19 damage. Whilst the glass fragments can be removed and
- 20 the retaining glass replaced, there is an interim risk of
- 21 injury to persons coming into contact with the broken
- 22 fragments.

- 24 Considerable research has been conducted to find
- 25 materials which can be used in Applications similar to
- 26 glass but which minimise the risk of damage to persons in
- 27 the instance of the material being broken either
- 28 intentionally or accidentally. Safety glass i.e.
- 29 toughened glass, materials are well known in the art and
- 30 have numerous applications and uses. Most have enhanced
- 31 safety by virtue of being reinforced in strength, such
- 32 that they have a higher stress to failure than glass; in
- 33 other words a greater force is needed to shatter or break
- 34 them than would be required with ordinary glass. Uses

1 vary from windows and doors on automobiles and public

- 2 transport, to domestic uses such as shower enclosures and
- 3 room partitions. Whilst in many instances these have
- 4 greatly increased safety, they are of limited use in
- 5 Applications where it is actually desirable for the glass
- 6 to be broken, i.e. when used on retaining boxes of
- 7 emergency apparatus and alarms, because of their enhanced
- 8 strength and resistance to force.

9

- 10 For example the polymeric materials Perspex<sup>™</sup> and
- 11 Plexiglas<sup>™</sup>, are transparent like glass, and do not pose
- 12 the same risk of injury when broken. However, these
- 13 materials can be harder to break than glass and can still
- 14 produce sharp fragments when broken.

15

- 16 In addition, the containers in which alcoholic drinks,
- 17 carbonated soft drinks and oxygen sensitive juices are
- 18 sold are also traditionally manufactured from glass.
- 19 Glass bottles are well received by consumers as they
- 20 impart the impression of a high quality product and have
- 21 "chink factor". Nevertheless, the use of bottles is
- 22 inherently dangerous, as glass is easily broken. It will
- 23 be appreciated that this is a particular problem in bars,
- 24 pubs and nightclubs, where accidental breakage of glass
- 25 bottles, is a potential health risk.

- 27 Glass bottles are also disliked as they can be used
- 28 deliberately, as weapons, to inflict damage on other
- 29 persons. In fact, safety regulators have actively
- 30 encouraged drinks manufacturers, as well as
- 31 establishments which serve drinks and alcohol, to use
- 32 bottles and glasses made from non-dangerous materials, in
- 33 order to reduce the number of serious injuries caused by
- 34 glass and bottle attacks.

1

- 2 In recent years there has been a move towards providing
- 3 bottles manufactured from materials which are not as
- 4 dangerous as glass. It is estimated that packaged beer
- 5 production world wide in 1996 was 106.6 billion litres,
- 6 requiring 186.2 billion bottles and 73.7 billion cans.
- 7 The beer bottle marker was forecasted to grow at an
- 8 annual rate of three percent through 2001 to 216 billion
- 9 units. Most bottle production makes use of glass with
- 10 only 0.1 billion plastic bottles being utilised in 1996.
- 11 However due to the push towards increased safety it is
- 12 estimated that the demand for plastic bottles is forecast
- 13 to reach 2.5 billion by 2006.

14

- 15 The focus on safer bottles is particularly important with
- 16 respect to alcoholic drinks, which are consumed in bars
- 17 and nightclubs. PET, poly(ethylene terephthalate), a
- 18 plastic which can be readily manufactured into bottles,
- 19 and which does not break as readily as glass, has already
- 20 been used for this purpose.

21

- 22 However the use of PET poses its own problems to the
- 23 industry. PET is a relatively expensive material and not
- 24 cheap to processwhich makes it a less popular option for
- 25 drinks manufacturers. In addition, there is a general
- 26 consensus that plastic bottles are not as well received
- 27 by the public as they feel cheaper and do not have the
- 28 same high quality feel as glass.

29

- 30 It is therefore an object of at least one aspect of the
- 31 present invention to provide a material which resembles
- 32 glass, but which has improved safety characteristics when
- 33 compared to ordinary glass.

1 It is also an object of at least one aspect of the

- 2 present invention to overcome the problems that are
- 3 described above with reference to existing glass and
- 4 plastic bottles.

5

- 6 According to a first aspect of the present invention
- 7 there is provided a material which shatters, when broken,
- 8 into fragments which do not cut, puncture or otherwise
- 9 damage human skin or tissue, wherein the material is
- 10 comprised of an amorphous thermoplastic polymer and one
- 11 or more low molecular weight resins.

12

- 13 Preferably the material is comprised of a simple mixture
- 14 of amorphous thermoplastic polymer and one or more low
- 15 molecular weight resins.

16

- 17 Preferably the amorphous thermoplastic polymer is chosen
- 18 from the group consisting of polystyrene (PS), polymethyl
- 19 methacrylate (PMAA), styrene-acrylonitrile copolymer
- 20 (SAN), linear polyesters and co-polyesters and
- 21 polycarbonate (PC).

22

- 23 The one or more low molecular weight resins chosen will
- 24 be completely compatible with the chosen polymer. For
- 25 example in the case of polystyrene the low molecular
- 26 weight resin is typically C9 aromatic hydrocarbon resin.

27

- 28 Preferably the material has a tensile stress limit of
- 29 between 11 and 60  $Nmm^{-2}$ .

- 31 Preferably the low molecular weight resin will have a Mn
- 32 (number average molecular weight) such that it has less
- 33 than 500 repeating units, and preferably less than 50
- 34 repeating units.

2 The material may be manufactured in sheet form.

3

- 4 According to a second aspect of the present invention
- 5 there is provided a polymeric blend comprising a polymer
- 6 selected from the group consisting of: polystyrene, (PS),
- 7 polymethyl methacrylate (PMAA), styrene-acrylonitrile
- 8 copolymer (SAN), linear polyesters and co-polyesters and
- 9 polycarbonate (PC) and one or more low molecular weight
- 10 resins.

11

- 12 The one or more low molecular weight resins chosen will
- 13 be completely compatible with the chosen polymer. For
- 14 example in the case of polystyrene the low molecular
- 15 weight resin is typically C9 aromatic hydrocarbon resin.

16

- 17 Preferably the one or more low molecular weight resins
- 18 have a Mn (number average molecular weight) such that it
- 19 has less than 500 repeating units, and preferably less
- 20 than 50 repeating units.

21

- 22 Preferably the one or more low molecular weight resins
- 23 are hydrocarbon resins.

24

- 25 Preferably the one or more low molecular weight resins
- 26 are aromatic hydrocarbon resins.

27

28 The polymeric blend may be manufactured in sheet form.

- 30 According to a third aspect of the present invention
- 31 there is provided a material which shatters, when broken,
- 32 into fragments which do not cut, puncture or damage human
- 33 skin or tissue, the material being comprised of
- 34 polystyrene and one or more low molecular weight resins.

2 Preferably the material is comprised of a simple mixture

3 of polystyrene and one or more low molecular weight

4 resins.

5

6 Preferably the one or more low molecular weight resins

7 are hydrocarbon resins.

8

9 Preferably the one or more low molecular weight resins

10 are aromatic hydrocarbon resins.

11

12 Most preferably the one or more low molecular weight

13 hydrocarbon resins are C9 aromatic hydrocarbon resins.

14

15 Preferably the one or more low molecular weight resins

16 are, or are derived from, alpha methyl styrene.

17

18 Preferably the one or more low molecular weight

19 hydrocarbon resins are selected from a group consisting

20 of; Norsolene™, Kristalex™, Plastolyn™ Endex™,

21 Piccotex™, Piccolastic™, Sukorez™ or Arkon™.

22

23 Most preferably the one or more low molecular weight

24 hydrocarbon resins are selected from a group consisting

25 of; Norsolene W90<sup>™</sup>, Norsolene W100<sup>™</sup>, Norsolene W110<sup>™</sup>,

26 Kristalex F85 <sup>™</sup>, Kristalex F100 <sup>™</sup>, Kristalex F115 <sup>™</sup>,

27 Plastolyn 240 <sup>™</sup>, Plastolyn 290 <sup>™</sup>, Endex 155 <sup>™</sup>,

28 Piccolastic D125 TM, Sukorez 100 TM, Sukorez 120 TM, Arkon

29 P100  $^{\text{TM}}$ , Arkon P125  $^{\text{TM}}$ , Arkon P140  $^{\text{TM}}$ , Piccotex 75  $^{\text{TM}}$ ,

30 Piccotex 100 <sup>™</sup> or Piccotex 120 <sup>™</sup>.

31

32 Preferably the one or more low molecular weight resins

33 will have a Mn (number average molecular weight) such

that it has less than 500 repeating units, and preferably

2 less than 50 repeating units.

3

4 Preferably the material has a tensile stress limit

5 between 11 and 60 Nmm<sup>-2</sup>.

6

7 Optionally the material may also include UV inhibitors,

8 antioxidants, flow modifiers, fire retarding agents,

9 colour pigments and brighteners as known in the art.

10

11 The material may be manufactured in sheet form.

12

13 According to a fourth aspect of the present invention

14 there is provided a method of manufacturing a material

15 which shatters, when broken, into fragments which do not

16 cut, puncture or damage human skin or tissue, the method

17 comprising the step of mixing an amorphous thermoplastic

18 polymer and one or more low molecular weight resins.

19

20 Preferably the amorphous thermoplastic polymer is chosen

21 from the group consisting of polystyrene (PS), polymethyl

22 methacrylate (PMAA), styrene-acrylonitrile copolymer

23 (SAN), linear polyesters and co-polyesters and

24 polycarbonate (PC).

25

26 Preferably the one or more low molecular weight resins

27 are completely compatible with the chosen polymer. For

28 example in the case of polystyrene preferably the chosen

29 low molecular weight resin is C9 aromatic hydrocarbon

30 resin.

31

32 Preferably the one or more low molecular weight resins

33 are hydrocarbon resins.

1 Preferably the one or more low molecular weight resins

2 are aromatic hydrocarbon resins.

3

4 Preferably the low molecular weight resin will have a Mn

5 (number average molecular weight) such that it has less

6 than 500 repeating units, and preferably less than 50

7 repeating units.

8

9 Preferably as the polystyrene is mixed with the one or

10 more low molecular weight hydrocarbon resins, the glass

11 transition temperature  $(T_g)$  of the material is elevated.

12 Typically the Tg is elevated to 5-10 degress C higher

13 than the base polymer.

14

15 According to a fifth aspect of the present invention

16 there is provided a method of manufacturing a material

17 which shatters, when broken, into fragments which do not

18 cut, puncture or damage human skin or tissue, the method

19 comprising the step of mixing polystyrene and one or more

20 low molecular weight hydrocarbon resins.

21

22 Preferably the one or more low molecular weight resins

23 are hydrocarbon resins.

24 ·

25 Preferably the one or more low molecular weight resins

26 are aromatic hydrocarbon resins.

27

28 Most preferably the one or more low molecular weight

29 hydrocarbon resins are C9 aromatic hydrocarbon resins.

30

31 Preferably the one or more low molecular weight resins

32 are, or are derived from, alpha methyl styrene.

- 1 Preferably the one or more low molecular weight
- 2 hydrocarbon resins are selected from a group consisting
- 3 of; Norsolene™, Kristalex™, Plastolyn™ Endex™,
- 4 Piccotex™, Piccolastic™, Sukorez™ or Arkon™.

- 6 Most preferably the one or more low molecular weight
- 7 hydrocarbon resins are selected from a group consisting
- 8 of; Norsolene W90<sup>™</sup>, Norsolene W100<sup>™</sup>, Norsolene W110<sup>™</sup>,
- 9 Kristalex F85 <sup>™</sup>, Kristalex F100 <sup>™</sup>, Kristalex F115 <sup>™</sup>,
- 10 Plastolyn 240 <sup>™</sup>, Plastolyn 290 <sup>™</sup>, Endex 155 <sup>™</sup>,
- 11 Piccolastic D125 TM, Sukorez 100 TM, Sukorez 120 TM, Arkon
- 12 P100 <sup>™</sup>, Arkon P125 <sup>™</sup>, Arkon P140 <sup>™</sup>, Piccotex 75 <sup>™</sup>,
- 13 Piccotex 100 <sup>™</sup> or Piccotex 120 <sup>™</sup>.

14

- 15 Preferably the low molecular weight resin will have a Mn
- 16 (number average molecular weight) such that it has less
- 17 than 500 repeating units, and preferably less than 50
- 18 repeating units.

19

- 20 The method may comprise the optional step of adding an
- 21 additive selected from the group consisting of UV
- 22 inhibitors, antioxidants, flow modifiers, fire retarding
- 23 agents, colour pigments and brighteners as known in the
- 24 art.

25

- 26 Preferably as the polystyrene is mixed with the one or
- 27 more low molecular weight hydrocarbon resins, the glass
- 28 transition temperature  $(T_q)$  of the material is elevated.
- 29 Typically the Tg is elevated to 5-10 degress C higher
- 30 than the base polymer.

- 32 According to a sixth aspect of the present invention,
- 33 there is provided a container manufactured from a
- 34 material that shatters when broken into fragments which

1 do not cut, puncture or otherwise damage human skin or

2 tissue.

3

4 The container may be a bottle, glass, tumbler, or the

5 like.

6

7 Preferably the material is comprised of an amorphous

8 thermoplastic polymer and one or more low molecular

9 weight resins.

10

11 Preferably the amorphous thermoplastic polymer is chosen

12 from the group consisting of: polystyrene (PS), styrene-

13 acrylonitrile co-polymer (SAN), linear polyesters and co-

14 polyesters polycarbonate (PC).

15

16 Preferably the one or more low molecular weight resins

17 are hydrocarbon resins.

18

19 Preferably the one or more low molecular weight resins

20 are aromatic hydrocarbon resins

21

22 The one or more low molecular weight resins chosen will

23 be completely compatible with the chosen polymer. For

24 example, in the case of polystyrene, the low molecular

25 weight resin will typically be C9 aromatic hydrocarbon

26 resin.

27

28 Preferably the material has a tensile stress limit

29 between 11 and 60 Nmm<sup>-2</sup>.

30

31 Preferably the one or more low molecular weight

32 hydrocarbon resins are selected from a group consisting

33 of: Norsolene™, Krystalex™, Plastolyn™, Endex™,

34 Piccotex™, Piccolastic™, Sukorez™, Arkon™

- 2 Most preferably the one or more low molecular weight
- 3 hydrocarbon resins are selected from a group consisting
- 4 of; Norsolene W90<sup>™</sup>, Norsolene W100<sup>™</sup>, Norsolene W110<sup>™</sup>,
- 5 Kristalex F85 <sup>™</sup>, Kristalex F100 <sup>™</sup>, Kristalex F115 <sup>™</sup>,
- 6 Plastolyn 240 <sup>™</sup>, Plastolyn 290 <sup>™</sup>, Endex 155 <sup>™</sup>,
- 7 Piccolastic D125 <sup>™</sup>, Sukorez 100 <sup>™</sup>, Sukorez 120 <sup>™</sup>, Arkon
- 8 P100 TM, Arkon P125 TM, Arkon P140 TM, Piccotex 75 TM,
- 9 Piccotex 100 <sup>™</sup> or Piccotex 120 <sup>™</sup>.

10

- 11 Preferably the low molecular weight resin will have a
- 12  $M_n$  (number average molecular weight) such that it has
- 13 less than 500 repeating units, and preferably less than
- 14 50 repeating units.

15

- 16 The container may be manufactured from the material using
- 17 injection blow moulding and/or injection stretch blow
- 18 moulding techniques.

19

- 20 Alternatively, the container may be manufactured from the
- 21 material using extrusion blow moulding.

22

- 23 Optionally the material of the container may also
- 24 comprise a oxygen barrier. The material of the container
- 25 may also comprise oxygen scavengers.

26

- 27 The barrier included in the material of the container may
- 28 be selected from the group consisting of: acrylonitrile-
- 29 methyl acrylate copolymer, ethylene vinyl alcohol (EVOH)
- 30 or nylon MXD6.

31

- 32 Preferably the barrier is Barex ™. Most preferably the
- 33 barrier is Barex™ 210 or Barex™ 218.

1 In the embodiment where nylon MXD6 is used as a barrier,

- 2 the oxygen scavenger may be X-312. Amosorb 3000, or a
- 3 scavenger of MXD6 with metal catalysed oxygen reduction

4 chemistry may also be used.

5

- 6 The barrier may be overmoulded or sprayed onto the
- 7 container or alternatively may be included in the
- 8 material of the container, using co-injection techniques.

9

- 10 The container may also have an inorganic coating. This
- 11 may be a thin layer of amorphous carbon. The inorganic
- 12 coating may be applied to the inside surface of the
- 13 container. Typically the inorganic coating will be
- 14 applied in a layer of 100 to 200nm thickness. The layer
- 15 may be applied by spraying.

16

- 17 The container may also have an external organic coating.
- 18 The external organic coating may be PVDC or a two
- 19 component epoxyamine.

20

- 21 The container may be manufactured from multiple layers of
- 22 the material. Two or more layers of the container may be
- 23 combined to act as an improved oxygen barrier.

24

- 25 Optionally the material of the container may also include
- 26 UV inhibitors, antioxidants, flow modifiers, colour
- 27 pigments and brighteners as known in the art.

28

- 29 Preferably as the amorphous thermoplastic polymer is
- 30 mixed with the one or more low molecular weight
- 31 hydrocarbons, the glass transition temperature is
- 32 elevated. Preferably the material of the container has a
- 33 glass transition temperature of above 80°C.

1 The material herein described can be used as a substitute

- 2 for ordinary glass. The material is glass-like in
- 3 character having clarity, brittleness, low strain to
- 4 failure and rigidity. The material has a variety of uses
- 5 including application as enclosures and boxes to house
- 6 emergency equipment e.g. keys, first aid boxes, fire
- 7 extinguisher, window hammers, emergency stop buttons,
- 8 emergency kick out panels and alarms, as well as use in
- 9 access panels, windows and doors. It should be
- 10 recognised that the abovedescribed uses are by way of
- 11 example only and are not intended to limit the manner in
- 12 which the material is used. The material can be
- 13 manufactured in sheet form, by extrusion, and moulded
- 14 into any shape by injection moulding or other standard
- 15 melt processes.

16

- 17 Table 1 shows the stress-strain behaviour of the material
- 18 in comparison to other polystyrene materials. Figure 1
- 19 shows this information in the form of a graph.

20

Table : Comparison of Properties of Safeglass™ to Polystyrenes.						
Polymer Type:	Modulus / GPa	Yield stress / MPa	Yield strain / %	Stress at break / MPa	Strain at break / %	Vicat softening temperature
Polystyrene (i.e. "crystal" or GPPS)	3.0 - 3.2	Brittle - no yield		4 75	2	82 - 98
Toughened polystyrene (e.g. HIPS)	1.6 - 2.4	18 - 38	1.5	< yield	15 - >50	76 -95
Safeglass <sup>TM</sup>	3.1 - 3.4	Brittle -	no yield	8 - 40	1 - 2	95 - 104

- 22 N.B. Safeglass<sup>™</sup> materials are slighly more rigid and
- 23 certainly more brittle than conventional
- 24 "crystal"polystyrene. Modified polystyrenes are
- 25 invariably less rigid and tougher materials as a result
- 26 of blending with a rubbery (low  $T_g$ ) additive. This also
- 27 results in a lowering of the Glass Transition Temperature

1  $(T_g)$  as witnessed by the reduction in the Vicat Softening

- 2 Temperature. The reverse is true of Safeglass™ materials
- 3 which show no such decrease in  $T_g$ , indeed it can be
- 4 higher than the critical temperature.

5

- 6 The material is fundamentally a blend of a rigid and
- 7 normally brittle amorphous thermoplastic with a glass
- 8 transition temperature Tg at least 5° C above ambient and
- 9 one or more compatible low molecular weight resins.

10

- 11 An example embodiment will now be described by way of
- 12 example only.

13

- 14 A rigid and normally brittle amorphous thermoplastic
- 15 polymer is blended with one or more low molecular weight
- 16 resins which have a Mn (number average molecular weight)
- 17 such that the resin has less than 500 repeating units,
- 18 preferably less than 50 repeating units. The one or more
- 19 low molecular weight resins have a weight average
- 20 molecular weight of 6050 or below.

21

- 22 The material is manufactured by mixing or blending a
- 23 clear polymer with one or more low molecular weight
- 24 hydrocarbon resins. The polymer is an amorphous
- 25 thermoplastic and can be chosen from the group of
- 26 polystyrene, (PS), polymethyl methacrylate (PMAA),
- 27 styrene-acrylonitrile copolymer (SAN), linear polyesters
- 28 and co-polyesters and polycarbonate (PC). It is important
- 29 that the low molecular weight resin is completely
- 30 compatible with the chosen polymer. For example in the
- 31 case of polystyrene it is C9 aromatic hydrocarbon resin.

32

33 In the herein described embodiment polystyrene is used.

1 The one or more low molecular weight resins which are

- 2 mixed with the polystyrene are aromatic hydrocarbon
- 3 resins and typically C9 aromatic hydrocarbon resins.
- 4 The one or more resins are typically alpha methyl styrene
- 5 or vinyl toluene or derivatives thereof. These are
- 6 selected from the following group: Norsolene W90TM,
- 7 Norsolene W100<sup>™</sup>, Norsolene W110<sup>™</sup>, Kristalex F85 <sup>™</sup>,
- 8 Kristalex F100 <sup>™</sup>, Kristalex F115 <sup>™</sup>, Plastolyn 240 <sup>™</sup>,
- 9 Plastolyn 290 <sup>™</sup>, Endex 155 <sup>™</sup>, Piccolastic D125 <sup>™</sup>, Sukorez
- 10 100 <sup>™</sup>, Sukorez 120 <sup>™</sup>, Arkon P100 <sup>™</sup>, Arkon P125 <sup>™</sup>, Arkon
- 11 P140 <sup>™</sup>, Piccotex 75 <sup>™</sup>, Piccotex 100 <sup>™</sup> or Piccotex 120 <sup>™</sup>.

12

- 13 It has been discovered that by blending polystyrene with
- 14 one or more of the abovementioned low molecular weight
- 15 hydrocarbon resins, a hard, rigid material is formed
- 16 which has the appearance and feel of glass, but which is
- 17 extremely brittle and has low strain to failure. The
- 18 material also has the inherent advantage that when
- 19 broken, unlike glass, the material breaks into fragments
- 20 which are not sharp and do not injure skin or tissue. The
- 21 material is, by design, manufactured to break between 11
- 22 and 60 Nmm<sup>-2</sup>. Therefore the material, when provided as a
- 23 substitute to glass, for example in retaining boxes for
- 24 emergency devices and alarms, can easily be broken by a
- 25 human hand, fist, elbow, foot or the like and
- 26 advantageously shatters into fragments or pieces which
- 27 are not sharp and are not capable of cutting or
- 28 puncturing human skin. Due to the inherent advantages of
- 29 the material it is envisaged that it may have a variety
- 30 of other uses, for example it may have application in
- 31 novelty toys, such as stress relief toys, or have uses in
- 32 "stunt" apparatus in, for example, theatres, shows or on
- 33 film sets.

- 1 The material is manufactured by conventional melt
- 2 compounding techniques. As the polystyrene is mixed with
- 3 the one or more low molecular weight hydrocarbon resins,
- 4 the glass transition temperature  $(T_g)$  of the material is
- 5 elevated as the low molecular weight resin does not have
- 6 a plasticising effect, the opposite effect is seen as the
- 7 glass transition temperature of the material is elevated.

- 9 The material is generally transparent or clear, however
- 10 dyes may be added to change the appearance of the
- 11 material.

12

- 13 Low molecular weight in resins is a function of the
- 14 length of the chains in the resin. In this case the
- 15 hydrocarbon resins have a very low molecular weight, too
- 16 low in fact for the resins to be of any use on their own,
- 17 and are difficult to mould. By mixing low molecular
- 18 weight hydrocarbon resin with polystyrene, the stress
- 19 limit of the polystyrene is reduced giving the material
- 20 the characteristics described in the present Application.
- 21 Preferably the low molecular weight resin will have a Mn
- 22 (number average molecular weight) such that it has less
- 23 than 500 repeating units, and preferably less than 50
- 24 repeating units.

25

- 26 The following is an example of the material of the
- 27 present invention.

- 29 Example 1
- 30 In order to achieve a material with a stress limit of 24
- 31 Mpa, a 50% mix of polymer and 50% resin is used, which
- 32 acheieves this stress limit. Typically the polymer could
- 33 be crystal polystyrene such as Polystyrol™ 143E, and
- 34 resin Plastolyn™ 240.

## 2 Example 2

3 In order to achieve a material with a stress limit of 34

18

- 4 Mpa, a 60% mix of polymer and 40% resin is used, which
- 5 acheieves this stress limit. Typically the polymer could
- 6 be crystal polystyrene such as Polystyrol™ 143E, and
- 7 resin Plastolyn™ 240.

8

- 9 A container having improved safety characteristics can be
- 10 manufactured from the material comprised of an amorphous
- 11 thermoplastic polymer and one or more resins. The resins
- 12 are aromatic hydrocarbon resins and are selected from a
- 13 group consisting of Norsolene <sup>™</sup>, Krystalex <sup>™</sup>, Plastolyn
- 14 <sup>™</sup>, Endex <sup>™</sup>, Sokorez <sup>™</sup>, Arkon <sup>™</sup>, Piccolastic<sup>™</sup> and
- 15 Piccotex™, and in particular Norsolene W90™, Norsolene
- 16 W100<sup>™</sup>, Norsolene W110<sup>™</sup>, Kristalex F85 <sup>™</sup>, Kristalex F100
- 17 <sup>™</sup>, Kristalex F115 <sup>™</sup>, Plastolyn 240 <sup>™</sup>, Plastolyn 290 <sup>™</sup>,
- 18 Endex 155 <sup>™</sup>, Piccolastic D125 <sup>™</sup>, Sukorez 100 <sup>™</sup>, Sukorez
- 19 120 <sup>™</sup>, Arkon P100 <sup>™</sup>, Arkon P125 <sup>™</sup>, Arkon P140 <sup>™</sup>, Piccotex
- 20 75 <sup>™</sup>, Piccotex 100 <sup>™</sup> or Piccotex 120 <sup>™</sup>. In a particular
- 21 embodiment the one or more low molecular weight resins
- 22 are C9 hydrocarbon resins with an  $\overline{M}_{n}$  (number average
- 23 molecular weight) such that it has less than 500
- 24 repeating units and preferably less than 50 repeating
- 25 units. The resin or resins chosen will be selected on
- 26 compatibility with the chosen polymer.

- 28 Low molecular weight in resins is a function of the
- 29 length of the chains in the resin. In this case the
- 30 hydrocarbon resins have a very low molecular weight, too
- 31 low in fact for the resins to be of any use as a
- 32 structural plastics material on their own, and are
- 33 difficult to mould. By mixing low molecular weight
- 34 hydrocarbon resin with polystyrene, the stress limit of

1 the polystyrene is reduced giving the material the

2 characteristics described in the present Application.

3

- 4 The amorphous thermoplastic polymer is chosen from the
- 5 group consisting of polystyrene (PS, styrene-
- 6 acrylonitrile co-polymer (SAN), linear polyesters and co-
- 7 polyesters and polycarbonate (PC). These can be mixed,
- 8 blended or polymerised with the one or more low molecular
- 9 weight resins. UV inhibitors, dyes, antioxidants, flow
- 10 modifiers, colour pigments and brighteners can also be
- 11 added to change or adapt the appearance of the container.

12

- 13 The container herein described has many characteristics
- 14 similar to an ordinary glass bottle i.e. clarity,
- 15 rigidity and brittleness. However when broken, the
- 16 bottle shatters into fragments which are harmless and
- 17 cannot be used to cut or pierce human skin.

18

- 19 The material used to manufacture the container is
- 20 fundamentally a blend of a rigid and normally brittle
- 21 amorphous thermoplastic with a glass transition
- 22 temperature Tq at least 50° C above ambient and one or
- 23 more compatible low molecular weight resins. A rigid and
- 24 normally brittle amorphous thermoplastic polymer is
- 25 blended with one or more low molecular weight resins
- 26 which have a  $\overline{M_n}$  (number average molecular weight) such
- 27 that the resin has less than 500 repeating units,
- 28 preferably less than 50 repeating units. The one or more
- 29 low molecular weight resins have a weight average
- 30 molecular weight of 6050 or below. The material is, by
- 31 design, manufactured to break between 11 and 60 Nmm<sup>-2</sup>.

- 33 The material can be heated and made into the desired
- 34 shape of the container, i.e. a bottle, glass or tumbler,

1 by any suitable technique known to the art e.g. injection

- 2 moulding, extrusion blow moulding or pre-form injection
- 3 blow moulding techniques.

4

- 5 The container may be manufactured from one or more layers
- 6 of the material. More than one layer may be used to
- 7 provide improved oxygen barrier characteristics.
- 8 Alternatively the container may be coated with an oxygen
- 9 barrier. Conventional coating technologies can be broadly
- 10 divided into two categories. The first are those that
- 11 use vacuum or plasma routes to deposit very thin films of
- 12 materials, such as carbon or silica, onto the surface of
- 13 the article being coated. The second, rely on the
- 14 atomised spraying of liquid organic materials onto the
- 15 external surfaces of the bottle. Ideally all coating
- 16 materials must not interfere with the economics of
- 17 recycling, nor detract from the bottle's appearance, but
- 18 a significant further consideration with thin film
- 19 internal deposits is the need for the materials to be
- 20 approved for food contact.

21

- 22 As the container described herein is manufactured from
- 23 the material at lower processing materials than
- 24 conventional plastics, barriers which are not usually
- 25 suitable for this purpose can be used. For example the
- 26 container can be coated in Barex™ (acrylonitrile-methyl
- 27 acrylate copolymer), and in particular Barex $^{\text{\tiny TM}}$  210 or
- 28 Barex™ 218, which has high oxygen barrier properties.
- 29 This can be achieved either by overmoulding, spraying or
- 30 co-injection techniques. The barrier could alternatively
- 31 be acrylonitrile-methyl acrylate copolymer, ethylene
- 32 vinyl alcohol (EVOH) or nylon MXD6. The barrier could be
- 33 provided on the inside or outside of the container.

1 Oxygen scavengers such as all polyester Amosorb 3000 or

- 2 X-312 scavenger may be used. These Oxygen scavenging
- 3 materials can be incorporated into the material of the
- 4 container to react with the gas before it reaches the
- 5 contents. Amosorb 3000 or X-312 scavenger have particular
- 6 application when the barrier selected is MXD6 nylon. With
- 7 these types of active oxygen scavenging packages, shelf
- 8 life performance is determined solely by the rate of
- 9 carbonation loss and CO<sub>2</sub> loss is reduced by the presence
- 10 of the MXD6 as a physical barrier. A scavenger of MXD6
- 11 with metal catalysed oxygen reduction chemistry may also
- 12 be used (Oxbar). This system reacts very quickly with
- 13 oxygen in the container and has a high oxygen capacity,
- 14 ensuring a long active life.

15

- 16 The container may also have an inorganic coating such as
- 17 amorphous carbon. This can be sprayed onto the surface
- 18 of the container being coated. The inorganic coating can
- 19 be applied either to the inside or outside of the bottle
- 20 after blowing. Plasma-applied coatings, using carbon or
- 21 silicon, which have recently been developed, may be used.
- 22 The Sidel Actis™ and Kirin DLC™ coating technologies can
- 23 be used produce a thin layer of amorphous carbon,
- 24 typically 100 to 200nm thick, on the inside surface of
- 25 the container. This is deposited from a high-energy
- 26 plasma of acetylene gas within a high vacuum environment.
- 27 The coating provides an excellent barrier to both O2 and
- 28 CO2, and, because it is on the inside of the container,
- 29 prevents the  $O_2$  dissolved in the material of the container
- 30 from migrating into the contents of the container during
- 31 the first few weeks of storage.

- 33 Because the deposited layers are fundamentally brittle,
- 34 they have to be extremely thin in order not to flake off

1 under container stresses, caused by bottle expansion and

- 2 creep when the bottle is filled, and under pressure from
- 3 the contents. Other factors include damage and scuffing
- 4 due to bottle handling, but these clearly do not affect
- 5 the integrity of the coating if it is on the inside. The
- 6 barrier performance improvements of carbon coatings are
- 7 similar to those achieved by organic coatings, again
- 8 giving a longer potential retail shelf life of around
- 9 nine months.

10

- 11 Silica technologies such as Glaskin and BestPet can also
- 12 be used. These rely on the application of a  $SiO_X$  vacuum
- 13 plasma coating, to give a barrier layer between 40 and
- 14 60nm thick. While the Glaskin process applies the glass
- 15 clear coating to the inside of the bottle, the BestPet
- 16 technique applies it to the outside.

17

- 18 As an alternative an organic coating may be used.
- 19 External organic coatings have been known and used in the
- 20 industry since the early 1980s. In the mid 1990s, barrier
- 21 coating solutions based on two component epoxyamine
- 22 chemistry (Bairocade) were developed, first to lengthen
- 23 the shelf life of the smaller soft drink sizes in hotter
- 24 climates, and then for beer. These provide a
- 25 transparent, glossy, external spray coating which is an
- 26 excellent barrier to migration of  $CO_2$  and  $O_2$ , and is
- 27 unaffected by humidity. The low temperature thermoset
- 28 cure provides a tough film, robust to filling and
- 29 handling conditions.

- 31 Typically the coating will be applied to the container at
- 32 thicknesses between  $6\mu m$  and  $10\mu m$ , and allow the use of
- 33 standard resins and preforms with existing injection and
- 34 blow moulding equipment. The use of such coatings

1 provides a performance improvement which is around 19

- 2 times better than an uncoated container and translates
- 3 into a longer retail shelf life. The external organic

4 coating may be PVDC two component epoxyamine.

5

- 6 The alternative approach to improving the gas permeation
- 7 properties of the container material is to manufacture it
- 8 from multiple layers of the material. In other words,
- 9 two or more layers of the container may be combined to
- 10 act as an improved oxygen barrier. Final shape blowing
- 11 produces a bottle with up to seven different polymer
- 12 layers, which either act as a physical barrier to gas
- 13 permeation, or are chemically active in scavenging oxygen
- 14 from the material of the container and intercepting
- 15 oxygen diffusing in from outside.

16

- 17 The material herein described has an elevated glass
- 18 transition temperature, which is much higher than the
- 19 glass transition temperature of, for example, PET. PET
- 20 has a glass transition temperature that is lower than the
- 21 pasteurisation temperature used in the beer industry. As
- 22 a result when PET is used in the manufacture of bottles,
- 23 creep may occur during filling. In other words the
- 24 material expands, which causes deformity of the bottle.
- 25 This problem is eliminated using the material herein
- 26 described as the glass transition temperature is above
- 27 the pasteurisation temperature used during filling.

- 29 Furthermore, bottles made from PET are generally filled
- 30 using flash pasteurisation, as opposed to full
- 31 pasteurisation, which the industry prefers. Full
- 32 pasteurisation is generally more efficient which results
- 33 in a longer shelf life for the product. However full
- 34 pasteurisation is not generally used with PET materials.

1 A particular advantage of the material herein described

- 2 is that because it has an elevated glass transition
- 3 temperature, it can withstand full pasteurisation.

4

- 5 It has been discovered that using the above described
- 6 material a container such as a bottle, glass or tumbler
- 7 can be manufactured which does not cut, puncture or
- 8 otherwise damage human skin or tissue when broken. In
- 9 other words, the container will shatter into harmless
- 10 fragments, shards or pieces when broken.

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- 12 A particular advantage of the container described herein,
- 13 lies in the fact that even though it does not shatter
- 14 into dangerous fragment when broken, it has a similar
- 15 quality feel as glass, and has improved aesthetic
- 16 qualities over existing plastics such as PET. The
- 17 material herein described for use in manufacturing a
- 18 container, is relatively light and glass-like to touch
- 19 and as it is a polymer is can be processed, for example
- 20 by including oxygen barriers during production.
- 21 Importantly, the material is thicker than an equivalent
- 22 PET bottle so has a more glass-like feel but can be
- 23 manufactured into containers without an increase in cost.

24

- 25 Potential uses of the container are not limited. For
- 26 example, the container may be used for beer, carbonated
- 27 soft drinks, oxygen sensitive juices, beverages or milk

28

## Example 1

- 31 An 85% mix of polystyrene polymer and 15% resin is used
- 32 to manufacture a bottle with improved safety
- 33 characteristics. The 15% resin maybe comprised of a
- 34 single resin selected from the group consisting of

Norsolene <sup>™</sup>, Krystalex <sup>™</sup>, Plastolyn <sup>™</sup>, Endex <sup>™</sup>, Sokorez <sup>™</sup>, Arkon <sup>™</sup>, Piccolastic<sup>™</sup> and Piccotex<sup>™</sup>, or may be a

- 3 combination of two or more of the above. Plastolyn  $^{\text{TM}}$  is
- 4 particularly suitable for this purpose. The resin or
- 5 resins are selected to achieve a desired molecular weight

6 range.

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- 8 Further modifications and improvements may be added
- 9 without departing from the scope of the invention herein
- 10 intended.

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